

# THE RESEARCH OF METHANOL+TOLUOL BINARIES MIXTURES DENSITY AT HIGH PRESSURES

Y.M.Naziev, V.H.Hasanov, J.Y.Naziev

Azerbaijan Technical University, Baku, Azerbaijan

Azerbaijan State oil Academy, Baku, Azerbaijan.

## **The resume**

The method of hydrostatic weighing determines of system methanol + toluol in a range of temperatures 290-500 K and pressure 0.1-60 MPa. The maximal error of measurement makes 0.08%.

## **Introduction**

The experimental research of thermal of substances in a liquid condition is one of the most important problems in modern thermophysics because, the theory of a liquid condition short is advanced. Studying of thermal properties of mixes of one – atomic alcohols and aromatic hydrocarbons makes one of the major problems of thermodynamics. Researches in this area are stimulated, first of all, by that the understanding of a nature and prosperities of these complex systems is necessary for the successful decision of many process proceed in blend.

To present time a plenty of experimental data about density of pull aromatic hydrocarbons [1] is saved up and methyl alcohol [2] data on density of binary mixes methanol+toluol in the literature are absent.

In the present work as us it was experimentally investigated P-ρ-T-X dependence of binary mixes methanol+toluol in a liquid phase in an interval of temperatures 290-500 K and pressures 0.1-58.9 MPa, though every one 25% mass concentration.

## **Experimental installation**

Measurement are carried out on the installation using a method of hydrostatic weighing, providing high accuracy of measurements at

comparative simplicity of preparation and realization of experiments. The basic circuit of experimental installation is submitted on fig 1. She consists of the following basic units: measuring device 7 for definition of density of liquids and gases at various pressure and temperatures; analytical weights of type VLA-200-M; electronno – watching system 2; mercury squeeze a vessel; systems for creation, maintenance and measurements of temperature and pressure 3, 4, 5, 8, 14, 16; systems for filling installation by a liquid 15.

The electronno – watching system being one of the basic units of installation, server to reduction of pendant system of the measuring device a suspension with the help of the electromagnetic coil 13.

The measuring device is the basic part of experimental installation. The basic circuit of the measuring device is submitted on fig 2. It consists of the head 3, 5, the measuring chamber 6 in which there is a pendant system and a researched liquid. The pendant system in turn consist of the core 16, a float 14 and connecting them brass strings 15. The measuring chamber is made of steel of mark 1X18N9T.

The measuring chamber 6 and the bottom part of the head 5 tightly incorporate by means of a groove and are established on holders 9 (see fig 1). The head of the measuring device 1, 3, 4, 5 is made of the titan of mark BT-6. With the purpose of liquidation of influence of external magnetic factors on all pendant system in the researched environment the holder supporting the measuring device, and adjusting screws also are made of the titan of mark BT-6. Supporting adaptation 2 by means of a groove is attached to the bottom part of the head and serves for adjustment of a level of the core which is included in the coil of the gauge 12 (see fig 1). To a float 14 becomes attached brass a string 15 and it is passed through supporting adaptation 2. the opposite end of a string incorporates to

the core 16. the ferromagnetic core from brass has diameter of 2 mm, height of 85.4 mm. The core in the bottom part at height has of 18 mm brad, adding on each side on 2 mm for an emphasis on the adaptation supporting 2. the core is entered in the top part of the head 3 which by means of six bolts 4 tightly incorporate to the bottom part of the head 5 measuring devices. All this is made with special accuracy that mangan fiber the string was not bend also elements of pendant system did not become soiled. Bent mangan fiber the string during research should not concern internal walls of supporting adaptation of the head and the measuring chamber bolts 9 (fig 1) the measuring part of installation is established in strictly vertical position.

The measuring chamber from below is connected by a tube 17 with square a vessel to the mercury, intended for division of a researched liquid with working substance boadpiston a manometer and transfer of pressure from press to a liquid. For maintenance of uniformity of a temperature field of the measuring device it piston in a casing 12 made from brass of mark Br. M5, having high theramat conductivity ability. Internal diameter of a casing of 45 mm, external 100 mm, height of 180 mm. The given temperature during experience is reached and supported by regulation of capacity of the heaters stacked in specially made two – section furuance 14 (see fig.1), put on a copper casing.

At measuring of density the head of installation usually keep at room temperature, or a little bit deviates from room. It is reached by square cooling water through the heat exchange 13 attached to the head from the bottom side. In the head the aperture in which the mercury thermometer is placed is stipulated, allowing to supervise stability of temperature of the head at transition from one isotherm to another.

At manufacturing details of the measuring device the special attention was given to coaxiality therefore they are made on special technologies. All surfaces of parts of the measuring device carefully were ground, and sharp corners were approximated. The core also ground and chrome plated.

Measurement of temperature of a researched liquid is the important condition of correct definition of its density.

The temperature of the measuring device with a researched liquid is measured by the platinum exemplary thermometer of resistance such as PTS-10, made in Moscow, with a margin error 0.05 K.

The sensitive element of the thermometer is executed from platinum of mark PL-1 with factor  $R_{100}/R_0=1.39240$ ;  $R_0=10.1792 \text{ Ohm}$ . For the control of uniformity of a field of temperatures of the measuring device with a researched liquid were used chromel–kopel thermocouples which are connected to a potentiometer of mark P363-1.

The temperature of the head with researched liquid is measured by a set of laboratory mercury thermometers with the price of division 0.1 K.

For creation and measurement of pressure it was used a piston manometer of MP2500 of a class of accuracy 0.05.

### **Realization of experiment**

The order of realization of experiments as usually, begins with preparation of experimental installation for work.

Before refueling by researched substance the system carefully is washed out and evacuated by means of the vacuum pump 17 (see fig.1). The weight of pendant system with the help of analytical weights VLA-200-M is determined. For this purpose the solenoid 13 with a current is weighed at a suspension of

pendant system and without it. Results of these weighing allow to determine weight of pendant system in vacuum, i.e. weight  $m_1$ . At correct assembly of experimental installation the weight of pendant system determined thus should coincide with results caliber measurements.

After, having closed the gate 18 and having opened 19, in the measuring device completely fill researched substance. Further researched substance deareate heating of a measuring part of installation to temperature of boiling of substance. Them top-blocker installation is closed also is checked on tightness by creation of the pressure exceeding the maximal value of pressure of experience.

After achievement of a stationary mode weighing the electromagnetic coil with pendant system and without it is made at the given temperature and the appropriate pressure. As a result of these weighings weight of pendant system in the researched environment is defined at the appropriate parameters of a condition of weighing at the fixed values of temperature and pressure made some times both at one, and at a return direction of a current through the solenoid. Then it is possible to pass to the following temperature and after achievement of a new stationary mode weighing is made at new value of temperature and various pressure. The size of a temperature interval between the next stationary modes made 20-25 K and on pressure 5-10 MPa.

At realization of experiments with first three isotherms tried to hold temperature of a zone of the core, that is the head, constant. It allowed to calculate values of density under the formula

$$\rho = \frac{m - (m_2 - m_1) (1 - \rho_a / \rho_w) - \rho_c (V_c + 0.5 V_t)}{V_f \delta_1 \delta_2 + 0.5 V_t}$$

As the density of a liquid in a zone of the core undertook by results of measurements on the first isotherm where the liquid in a zone of

the core and a float was identical and paid off on the basic of the formula

$$\rho = \frac{m - (m_2 - m_1) (1 - \rho_a / \rho_w) - \rho_c (V_c + 0.5 V_t)}{V_f \delta_1 \delta_2 + V_c + V_t}$$

Here  $m = 9.0010 \text{ g} \pm 2.21 \cdot 10^{-4} \text{ g}$ ;  $V_f = 3.1212 \text{ cm}^3 \pm 3.61 \cdot 10^{-4} \text{ cm}^3$ ;  $V_c = 0.2647 \text{ cm}^3$ ;  $V_c = 0.2647 \text{ cm}^3 \pm 2.01 \cdot 10^{-4} \text{ cm}^3$ ;  $V_t = 0.039 \text{ cm}^3 \pm 15 \cdot 10^{-4} \text{ cm}^3$  - are defined by calibration with use than a liquid which density is known with a high degree of accuracy is more modeling;  $V_f$ ,  $V_c$ ,  $V_t$  - accordingly volume of a float, the core and a pendant thread in normal physical conditions,  $m_1$  and  $m_2$  - weight of weights, equilibrating in air the solenoid with pendant system and accordingly without it;  $\rho_w$  - density of a material of which weights are made,  $\rho_a$  - density of air,  $\rho_c$  - density of the core,  $\delta_1 = 1 + 3\alpha \cdot \Delta T$ ,  $\delta_2 = 1 - k \cdot \Delta P$ ,  $\alpha = 0.43 \cdot 10^{-6} \text{ K}^{-1}$  - factor of thermal linear expansion of quartz,  $k = 2.7 \cdot 10^{-5} \text{ MPa}^{-1}$  - factor of compressibility of quartz.

Temperature of a liquid in a zone of the core on first three isotherms supported constant intensity squeeze waters through heat the head of installation.

At higher temperatures, usually in higher 343.15 K to maintain temperature in a zone of the core of a constant became inconvenient. Therefore, for isotherms is higher 343.15 K than value and  $\rho_c$  undertook from the diagram constructed on the basis of three isotherms.

Experimental data on density of binary mixes methanol+toluol are gotten in tab.1.

### **Conclusions.**

All experimental results were analysis the detailed analysis of concentrated dependence P- $\rho$ -T-X of the given investigated systems has shown, that dependence of density on concentration deviates a line of additivity and changes with change of temperature and pressure.

**Table 1. Density of binary systems methanol+toluol ( $\rho$ , kg/m<sup>3</sup>)**

T, K	P, Mpa							
	0.1	5	9.9	19.7	29.5	39.3	49.1	58.9
Toluol								
298.15	863.0	867.0	870.7	877.7	884.5	890.7	869.5	901.9
323.15	839.6	844.0	848.1	856.1	863.4	870.7	877.0	883.2
348.15	915.5	820.6	825.6	835.0	843.6	851.3	858.5	865.3
373.15	-	797.3	803.2	813.9	823.4	832.0	839.9	847.4
398.15	-	772.2	779.4	791.8	803.0	812.4	821.5	829.4
423.15	-	745.4	753.9	768.8	781.1	792.1	802.5	811.6
448.15	-	718.4	729.0	746.2	760.5	772.9	784.0	794.0
473.15	-	689.2	702.3	722.3	739.4	753.0	765.5	776.0
498.15	-	657.5	674.3	699.0	717.9	733.8	746.9	758.0
75% methanol+25% toluol								
293.15	812.4	816.3	820.9	828.6	835.9	843.0	849.4	855.2
314.54	793.2	797.6	802.4	810.4	818.4	825.6	833.0	839.0
335.2	-	778.7	783.1	792.4	801.4	809.2	816.7	823.8
353.16	-	760.0	765.2	775.6	785.3	794.0	801.7	810.0
373.06	-	737.4	743.6	756.0	766.8	776.8	785.4	794.0
394.24	-	711.5	719.0	734.0	746.2	757.4	766.7	776.4
412.56	-	685.5	695.0	713.4	727.4	739.6	749.7	760.6
433.55	-	651.8	666.0	687.5	705.0	718.5	729.5	742.0
454.46	-	615.5	634.0	661.4	681.7	696.8	710.0	723.4
475.05	-	568.0	599.5	632.2	655.3	672.6	689.0	704.0
496.65	-	486.4	552.9	600.0	627.7	647.2	666.5	683.5
50% methanol+50% toluol								
291.65	831.0	835.3	839.5	846.8	854.0	860.5	866.7	872.8
312.25	812.5	816.9	821.4	829.4	841.3	848.4	855.0	861.0
333.56	-	797.2	802.0	811.0	819.5	827.3	834.5	840.8
352.15	-	778.4	784.0	794.3	803.7	812.2	819.6	826.7
372.05	-	756.2	763.4	776.0	786.4	795.3	803.4	811.0
390.38	-	734.5	743.0	758.0	770.0	779.6	788.2	796.4
414.74	-	700.5	712.3	731.4	745.2	756.6	766.4	775.8
435.17	-	667.6	683.0	706.2	722.5	735.8	747.2	757.8
453.15	-	639.0	656.0	682.1	711.5	716.7	729.7	741.1
475.34	-	594.5	620.4	651.5	673.4	691.0	706.5	720.4
498.05	-	528.3	575.4	616.3	642.4	663.4	680.6	697.5
25% methanol+75% toluol								
292.65	848.3	852.4	856.2	863.6	870.7	877.0	883.0	888.6
314.54	828.4	832.5	836.4	844.6	852.5	859.4	865.6	872.0
335.2	-	813.4	817.8	827.0	835.4	843.0	850.0	856.6
353.16	-	795.4	800.6	811.5	820.4	828.5	836.0	842.7
373.06	-	774.5	780.6	792.8	803.5	812.7	820.8	828.0
394.24	-	750.0	758.0	772.3	785.0	795.0	803.6	811.8
412.56	-	725.8	735.9	754.0	767.1	778.7	788.3	797.0
433.55	-	698.0	710.3	732.0	746.7	760.0	770.7	779.8
454.46	-	666.4	682.0	707.0	724.0	740.0	752.0	761.7
475.05	-	634.3	652.0	680.5	701.0	719.3	731.2	743.4
496.65	-	590.0	612.5	646.0	672.0	692.5	706.7	721.0

Generalization of experimental data is of interest from the point of view of storage of the information as the equation and forecasting of properties of investigated object. On internship for calculation of the tabulated data are widely used empirical and the equations of a condition. The analysis of an experimental material shows, that for the investigated substances is suitable the equations [3].

$$\rho^4 = A + B \cdot p^{0.5} + C \cdot P \quad (1)$$

where P-pressure MPa,  $\rho$ -density of substances g/cm<sup>3</sup>; A, B, C-coefficients, dependent on temperature, K.

Factors A, B, C are calculated for each isotherms by a method of the least squares and described in an analytical kind

$$A = \sum_{i=0}^5 a_i T^i; \quad B = \sum_{i=0}^6 b_i T^i; \quad C = \sum_{i=0}^6 c_i T^i \quad (2)$$

Values  $a_i$ ,  $b_i$ ,  $c_i$  – are given in table 2.

The equations (1) in view of dependences (2) are described with all file of experimental data with an overage error 0.05-0.1%.

## LITERATURE

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**Table 2.Coefficients of the equations (2) for  
toluol and methanol solutions.**

I	Toluol		
	a <sub>i</sub>	b <sub>i</sub>	c <sub>i</sub>
0	-0.91123683698	-39.36222473369	4.31016633496
1	2.0066881114·10 <sup>-2</sup>	0.629592835447	-6.8867859605·10 <sup>-2</sup>
2	-8.3405130549·10 <sup>-5</sup>	-4.1551509324·10 <sup>-3</sup>	4.54319706599·10 <sup>-4</sup>
3	1.2451680888·10 <sup>-7</sup>	1.4483605412·10 <sup>-5</sup>	-1.58339167296·10 <sup>-6</sup>
4	-3.9386124032·10 <sup>-11</sup>	-2.812590845·10 <sup>-8</sup>	3?075223236·10 <sup>-9</sup>
5	3.959517061·10 <sup>-14</sup>	2.88577744·10 <sup>-11</sup>	-3?1563825246·10 <sup>-12</sup>
6		-1.2224922489·10 <sup>-14</sup>	1?337861606·10 <sup>-15</sup>
75% methanol+25% toluol			
0	34.2706702064	38.08868515129	-2.90370649824
1	-0.4558690916	-0.6146222311	4.71554817167·10 <sup>-2</sup>
2	2.4547637008·10 <sup>-3</sup>	4.1213442074·10 <sup>-3</sup>	-3.18162679222·10 <sup>-4</sup>
3	-6.5751490806·10 <sup>-6</sup>	-1.4694675302·10 <sup>-5</sup>	1.141700583373·10 <sup>-6</sup>
4	8.724091989·10 <sup>-9</sup>	2.9370087907·10 <sup>-8</sup>	-2.2967549909·10 <sup>-9</sup>
5	-4.5895246345·10 <sup>-12</sup>	-3.1184249832·10 <sup>-11</sup>	2.4544423128·10 <sup>-12</sup>
6		1.3736879896·10 <sup>-14</sup>	-1.0880759666·10 <sup>-15</sup>
50% methanol+50% toluol			
0	29.42922764968	70.2573900928	-6.81163376566
1	-0.3883249041	-1.10953874199	0.107213361869
2	2.083842861·10 <sup>-3</sup>	7.2698563724·10 <sup>-3</sup>	-6.9980469747·10 <sup>-4</sup>
3	-5.5609512069·10 <sup>-6</sup>	-2.5296313555·10 <sup>-5</sup>	2.425390326·10 <sup>-6</sup>
4	7.3379597707·10 <sup>-9</sup>	4.92961988·10 <sup>-8</sup>	-4.707350355·10 <sup>-9</sup>
5	-3.831085516·10 <sup>-12</sup>	-5.09999017408·10 <sup>-11</sup>	4.8504605104·10 <sup>-12</sup>
6		2.1878537184·10 <sup>-14</sup>	-2.0726618165·10 <sup>-15</sup>
25% methanol+75% toluol			
0	16.407568806	117.0681909129	-11.2093465435
1	-0.2041938256	-1.8336785327	0.1754902225
2	1.05696582·10 <sup>-3</sup>	1.189503495·10 <sup>-2</sup>	-1.137525317·10 <sup>-3</sup>
3	-2.727215363·10 <sup>-6</sup>	-4.0903376629·10 <sup>-5</sup>	3.90811907903·10 <sup>-6</sup>
4	3.465893313·10 <sup>-9</sup>	7.863016373·10 <sup>-8</sup>	-7.5053502956·10 <sup>-9</sup>
5	-1.734435923·10 <sup>-12</sup>	-8.010678261·10 <sup>-11</sup>	7.6384604356·10 <sup>-12</sup>
6		3.378600624·10 <sup>-14</sup>	-3.218305825·10 <sup>-15</sup>

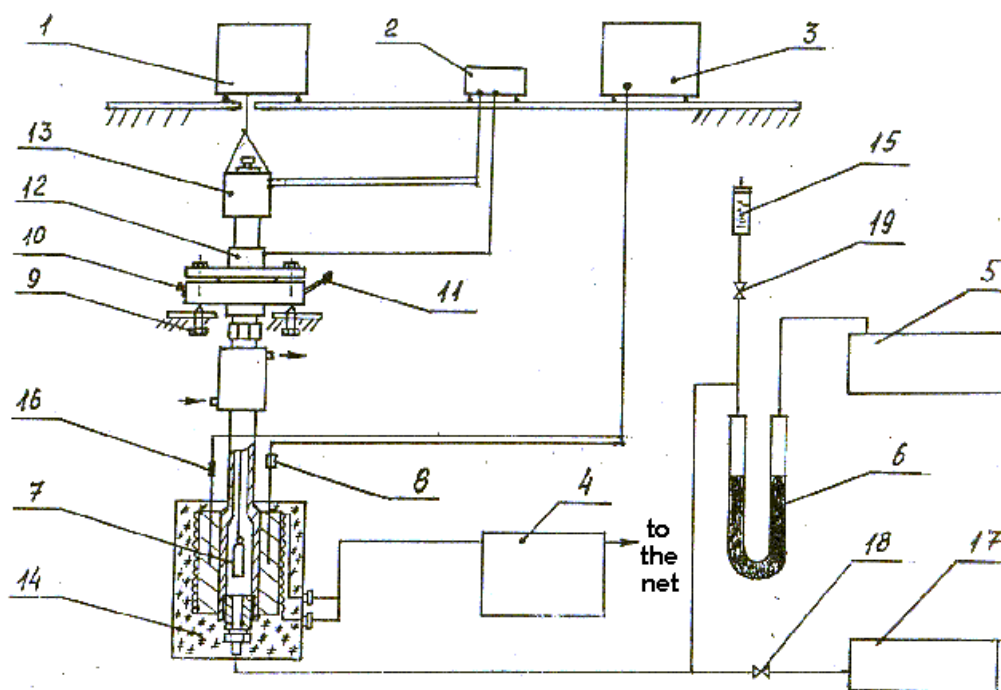


Fig 1. Of installations the definition of density of liquids:

1 - BLA-200 g-M type analytical balance; 2 - elektronno-observant system; 3 - potentiometer (P 363-1); 4 - regulator of a pressure (RNO); 5 - press (MP-600); 6 - mercury; 7 - part of the size of the equipment; 8 - the thermometer of resistance; 9 - bolt-regulator; 10 - balance; 11 - the thermometer; 12 - transmitting coil; 13 - electromagnet the coil; 14 - heater; 15 - glass vessel; 16 - the thermocouple; 17 - the vacuum pump; 18, 19 - the crane;

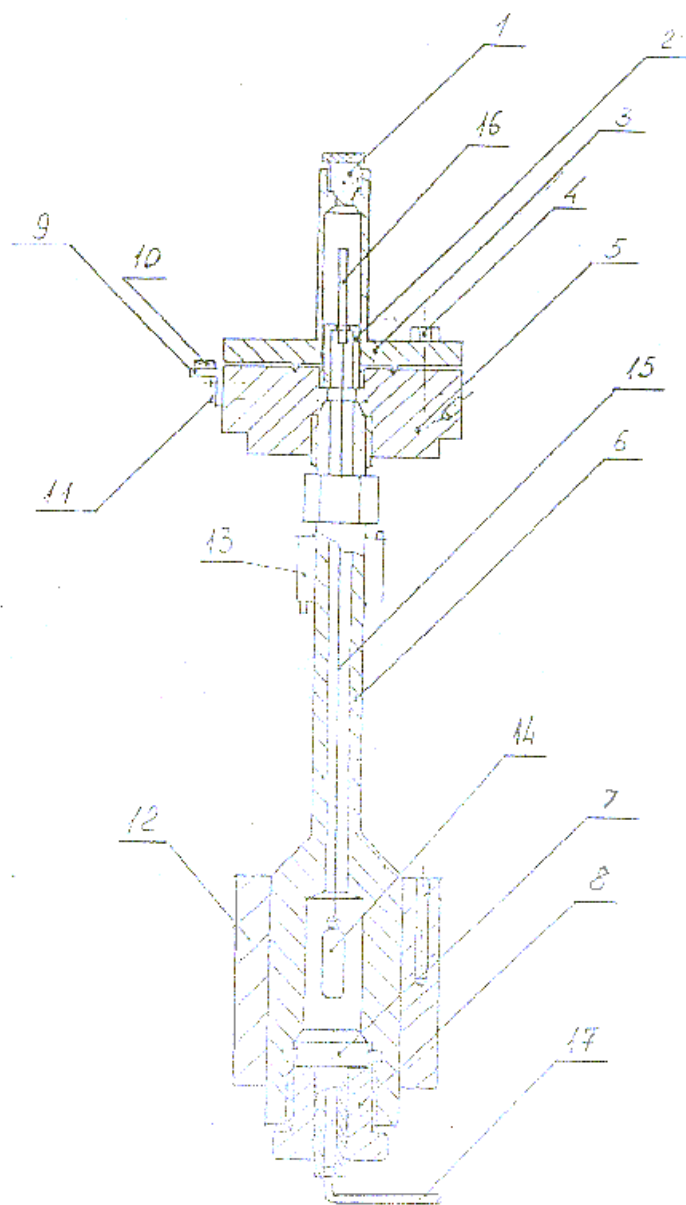


Fig 2.The measuring device of installation the definition of density of liquids.